



## Development of polyelectrolyte sulfonated chitosan-alginate as an alternative methanol fuel cell membrane

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Received 28 August 2020; Accepted 2 April 2021

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### ABSTRACT

The aim of this research is the development of biopolymers-based polyelectrolyte membranes (PEMs) for application in the fuel cell. The sulfonated chitosan derivatives and alginate base membranes are the parent biopolymer candidates used in this study to develop physically and chemically polyelectrolyte membranes fuel cell (PEMFC). The calcium alginate base membranes interact via ionic bonds with the sulfonated chitosan derivatives of different sulfonation degrees to have physically polyelectrolyte membranes. Activation of the calcium alginate base membranes with glutaraldehyde induced further covalent bonds in addition to the ionic ones during the reaction with the sulfonated chitosan derivatives of different sulfonation degrees to have chemically polyelectrolyte membranes. The developed PEMs were evaluated using Fourier-transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction and thermal gravimetric analysis analyses. Moreover, their ion exchange capacity, methanol permeability, young modulus analysis, and water uptake characters were measured. The developed chemically PEMFC show superior characters regard the physical counterpart. Moreover, the developed chemically PEMFC show comparable characters to the Nafion 117 membrane which encourages nominating the finding formulations for further PEMs developments.

*Keywords:* Sulfonated chitosan; Alginate; Polyelectrolyte membrane; Direct methanol fuel cell; Ions exchange capacity; Methanol permeability

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### 1. Introduction

The direct methanol fuel cell (DMFC) is a device converting chemical energy to electrical power instead of fossil fuel energy. Nowadays, DMFC are used in various portable power applications [1] such as a source for transportation and other portable applications (mobile phones, space, and

laptops) [2]. The enhancement of DMFC via improving the electrolyte membrane and the effectiveness of the catalysts has been studied by many researchers for several decades. The increase of the fuel cell performance resulted from the polymer electrolyte membrane modification to obtain low methanol permeability and higher proton conductivity. The accessible membrane that is used to date is a Nafion

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membrane as the electrolyte, which is composed of per-fluorinated sulfonic acid and although these membranes have sufficient physical and chemical stability along with their high proton conductivity, it has some disadvantages. First of all, it is an expensive material costing about \$600–1,200 per square meter [3]. In addition it has high methanol permeability, leading to methanol crossover as much as 40% from anode to the cathode that poisons the cathode and, consequently, affects the performance of the DMFCs [4,5] during the operation [6]. There are many research works on the development of methanol impervious membrane electrolytes for DMFCs. In recent years, natural and synthetic-polymer membranes have made a significant impact as polymer electrolytes for DMFCs [7–9] that are low-cost polymers that have high proton conductivity and low methanol permeability.

One of which is chitosan, which has been investigated widely in this application [10,11]. The limitation of chitosan solubility in neutral and alkaline pH restricts its use in several applications. Several derivatives of water-soluble chitosan were prepared, such as carboxylation, sulfonation, phosphorylation, etc. While chitosan and sulfonated chitosan had many excellent properties as a result of their functional groups, however, the membrane form has poor mechanical properties [12] because of its ionic behavior of amine and sulfonic groups of sulfonated chitosan [13].

Crosslinked chitosan showed promising characters and presented as a polyelectrolyte membrane fuel cell (PEMFC) [6,14]. Different approaches have been used to provide chitosan with the essential needs for PEMFC such as the addition of polymers [15]. Composites formation with inorganic materials is a promising technique to have excellent methanol barrier properties [16–19]. The recent advances in the application of chitosan in fuel cells have been reviewed [20].

Another polymer such as alginate has been fabricated in different forms for a variety of applications [21].

Blending chitosan and alginate to have a polyion complex presented very promising PEMFC with the essential characters [22]. Consider the advantages of the obtained results; novel polyelectrolyte membranes were prepared by replacing the chitosan with carrageenan (Car) which contains sulfonic groups in its structure contribute mainly to the ionic conductivity of the developed polyelectrolyte membranes (PEMs). The methanol permeability and proton conductivity of Alg/Car membranes increased with increasing carrageenan content [23].

Shaari and Kamarudin [10] reviewed the chitosan and alginate types of bio-membrane in FC. Muhmed et al. [24] reviewed the emerging chitosan and cellulose green materials for ion exchange membrane fuel cell.

Recently, sulfonated chitosan drives much attention in the application as a base of PEMFC due to its ionic conductivity and methanol parries characters [25–27]. Shirdast et al. [25] studied the effect of the incorporation of sulfonated chitosan/sulfonated graphene oxide on the proton conductivity of chitosan membranes. Wafiroh et al. [26] studied the production and characterization of sulfonated chitosan-calcium oxide composite membranes for PEMFC. Karuppaiah et al. [27] studied the synthesis and characterization of sulfonated chitosan/PEO-based polymer electrolyte membranes for fuel cell applications.

The PEMFC promising characters of the sulfonated chitosan and alginate inspired the authors to study the combination of both polymers to benefits from their characters, especially its higher ionic conductivity, as novel PEMFC. In our previous work, we developed low-cost chitosan and glutaraldehyde activated alginate for PEMFC applications using combined ionically and chemically crosslinking processes for the first time. The chitosan was chemically crosslinked using glutaraldehyde activated alginate (AlgG) macro-crosslinker to obtain PEMFC with 170% maximum ion exchange capacity (IEC) of the ionic crosslinked counterpart with the same molar ratio. Also, the obtained membranes have a lower permeability for methanol than Nafion membranes [28].

In this study, the glutaraldehyde activated alginate (AlgG), as a macro-crosslinker, used in crosslinking of the chitosan derivative, sulfonated chitosan (SC), to have covalent crosslinked alginate-GA-sulfonated chitosan (SC/AlgG) polyelectrolyte membranes for the first time and compared with the physically crosslinked counterpart (SC/Alg) to show the effect of the chemical cross-linking process. The physically crosslinked SC/Alg polyelectrolyte membranes have mainly ionic bonds result from the interaction between the alginate carboxylic groups from one side and the chitosan amine groups from another side as proposed in Fig. 1. On the other hand, the covalent crosslinked SC/AlgG polyelectrolyte membranes have a mix between the ionic bonds as in the physical counterpart in addition to chemical bonds between the glutaraldehyde activated alginate (AlgG) from one side and the sulfonated chitosan amine group from another side, Fig. 1. The developed polyelectrolyte membranes were characterized by scanning electron microscopy (SEM) to investigate the morphological structure, Fourier-transform infrared spectroscopy (FTIR) to verify the structure of the membranes, X-ray diffraction (XRD) to observe the crystallinity and tensile testing for mechanical stability. The basic requirements for the PEMFC were evaluated by measuring the water uptake, IEC, and methanol permeability. Finally, the efficiency of the developed membranes, as the ratio between IEC and methanol permeability, compared with the virgin Nafion membrane.

## 2. Experimental

### 2.1. Materials

Chitosan from crab shells (highly viscous) and 1,3-propane sultone was supplied by Sigma-Aldrich (USA). Sodium alginate (low viscous) was purchased from ALPHA (Germany). Glutaraldehyde (50%) was purchased from Polskie Odczynniki Chemiczne S.A. (Finland). Methanol (purity 99.8%) was purchased from Fluke Chemie GmbH (Switzerland). Sulfuric acid (purity 95%–97%) was provided by Sigma-Aldrich (Germany). Sodium hydroxide and phenolphthalein were purchased from El-Nasr Pharmaceutical Co. for Chemicals (Egypt).

### 2.2. Methods

#### 2.2.1. Preparation of sulfonated chitosan derivative

Sulfonated chitosan (SC) was prepared, according to the Tsai et al. method [29]. In a 250 mL round flask, 10 mM

chitosan (Ch) was dispersed in 50 mL of methanol, and different amounts of 1,3-propane sultone (5, 10 and 20 mM) were added. The mixture was stirred and heated at 65°C for 4 h under reflux conditions (Fig. 2). In the end, the reaction was stopped by cooling. The product was filtrated and washed several times with methanol to remove unreacted propane sultone. The resultant SC powder was collected and dried overnight in a vacuum oven. The sulfonated chitosan was obtained as a yellow powder in a yield of around 85%. Three different molar ratios of chitosan and 1,3-propane sultone were prepared and coded as SC0.5, SC1 and SC2, respectively.

### 2.2.2. Membrane preparation

Sodium alginate membrane was prepared by dissolving 1 g of sodium alginate in 100 mL distilled water.

Then, the solution was cast onto a clean glass plate and let to dryness at room temperature. The dry film thus formed was immersed into a solution of calcium chloride 2% or calcium chloride 2% and glutaraldehyde at 50°C for 3 h to obtain the alginate and glutaraldehyde activated alginate membranes. The sulfonated chitosan solutions (2%) with different degrees of sulfonation SC0.5, SC1 and SC2 were prepared by dissolving 2 g of the sulfonated chitosan in 100 mL distilled water. In order to prepare the PEMs, the alginate and glutaraldehyde-activated alginate membranes were then immersed in the sulfonated chitosan solutions for 3 h at room temperature. After that, the membranes were taken out, washed several times using pure water to eliminate any un-bounded residual of the sulfonated chitosan solutions, and dried at room temperature. Finally, two sets of PEMs were obtained. The first set is composed of three different physically alginate-sulfonated chitosan

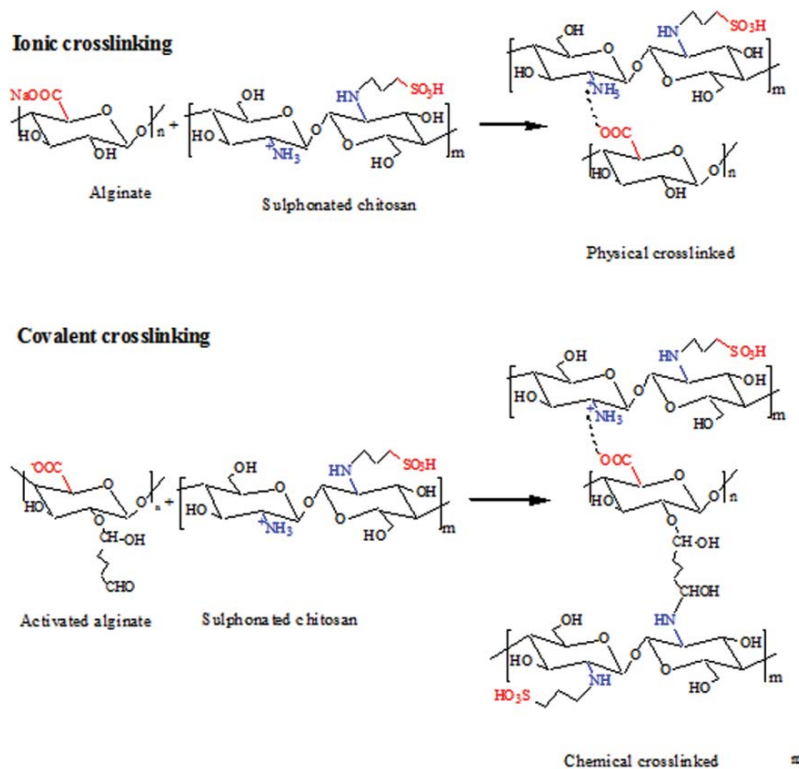


Fig. 1. The possible physical and chemical interactions between the alginate, glutaraldehyde activated alginate and the sulfonated chitosan.

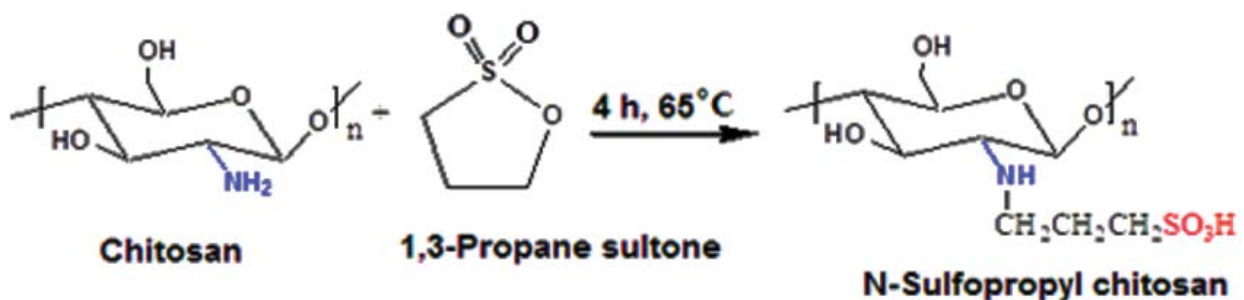


Fig. 2. Preparation of sulfonated chitosan (N-sulfopropyl chitosan).

PEMs coded as SC0.5/Alg, SC1/Alg and SC2/Alg in addition to the neat ionic crosslinked alginate membrane (Alg). The second set is composed of three different chemically SC/AlgG PEMs coded as SC0.5/AlgG, SC1/AlgG and SC2/AlgG in addition to the neat glutaraldehyde activated alginate membrane (AlgG).

## 2.3. Materials characterization

### 2.3.1. Elemental analysis

The percentages of carbon, nitrogen, hydrogen, and sulfur elements of SC were evaluated using an elemental analysis instrument (Elementar Vario EL III).

### 2.3.2. Fourier-transform infrared spectroscopy

The chemical structures of the prepared SC and the physical (SC/Alg) and chemical (SC/AlgG) formed PEMs were characterized with Fourier-transform infrared spectroscopy (Shimadzu FTIR-8400S, Japan) and the data were analyzed using the IR Solution software, version 1.21. The polymer sample (1–2 mg) was added to KBr (200 mg) and scanned between 4,000 and 400  $\text{cm}^{-1}$  using 30 scans at a resolution of 4  $\text{cm}^{-1}$ .

### 2.3.3. Thermal gravimetric analysis

The thermal stability and properties of the prepared SC and the physical (SC/Alg) and chemical (SC/AlgG) formed PEMs were measured with a thermo-gravimetric analyzer (Shimadzu TGA-50, Japan with a heating rate of 10°C/min in the temperature range from 25°C to 600°C under a continuous nitrogen flow of 20 mL/min.

### 2.3.4. Scanning electron microscopic analysis

The morphology of the prepared SC and the physical (SC/Alg) and chemical (SC/AlgG) formed PEMs was followed by scanning electron microscopy (JOEL 6360LA, Japan). The analyzed samples were fixed on a specimen mount with carbon paste. The surface of samples was coated with a thin layer of gold using a vacuum sputter coater to eliminate the poor conductivity of the sample's current before testing.

### 2.3.5. X-ray diffraction analysis

The change of the prepared SC and the physical (SC/Alg) and chemical (SC/AlgG) formed PEMs structure, under different polyion complexation conditions was investigated with a wide-angle X-ray diffractometer (Model Shimadzu 7000) angles ( $2\theta$ ) ranged from 2° to 50°.

### 2.3.6. Water uptake (%)

Dried membrane sample (3  $\text{cm}^2$ ) soaked in pure water at ambient temperature for 48 h. The swollen sample was withdrawn, and the excess of water was quickly wiped with tissue paper and the water uptake (%) was calculated using the following equation:

$$\text{Water uptake (\%)} = \frac{W - D}{D} \times 100 \quad (1)$$

where  $W$  and  $D$  are the weights of the wet and the dry membranes.

### 2.3.7. Ion exchange capacity

The interactive groups for the CS and the physical (SC/Alg) and chemical (SC/AlgG) PEMs were determined by a titration method [30]. The samples were soaked in 25 mL of 0.01 N sodium hydroxide solution for 1 d at ambient temperature. Then, the solution was titrated against 0.01 N sulfuric acid. The IEC was calculated according to the equation:

$$\text{IEC} = \frac{[(V2 - V1)a]}{w} \quad (2)$$

where  $V2$  and  $V1$  are the volumes of NaOH solutions required for complete neutralization of  $\text{H}_2\text{SO}_4$  in the absence and presence of the polymer, respectively, and ( $a$ ) is the normality of NaOH and ( $w$ ) is the weight of sample taken for analysis.

### 2.3.8. Methanol permeability

Methanol permeability experiments were carried out using a glass diffusion cell (Fig. 3) according to the method mentioned elsewhere [31]. The methanol permeability ( $P$ ) calculated according to the following equation [32];

$$P = \frac{(\alpha \times VB \times L)}{(S \times CA)} \quad (3)$$

### 2.3.9. Tensile strength measurement

The equipment used for carrying out the test was LLOYD Instruments LR10K (Shimadzu, Japan). The mean of three measurements values was performed at least for

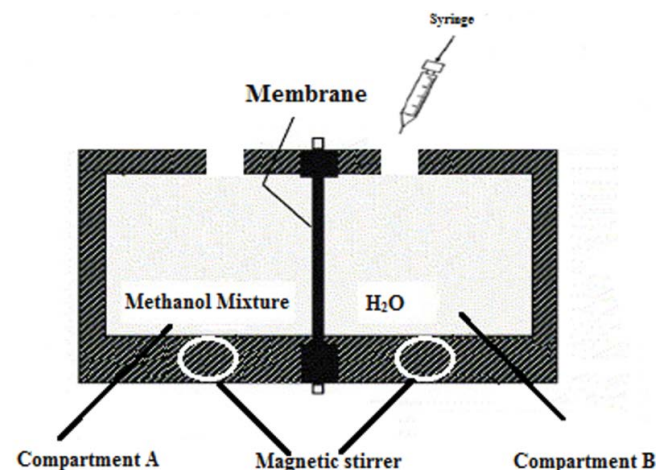


Fig. 3. Glass diffusion cell for methanol crossover measurements.

each sample. Tensile strength was calculated using the equation:

$$\text{Tensile strength} = \frac{\text{Max Load}}{\text{Cross-sectional area (N/mm}^2\text{)}} \quad (4)$$

#### 2.3.10. Thermomechanical analysis

The change in membrane thickness while subjected to constant load (5 g) at a temperature range (ambient to 120°C) was measured with the thermomechanical analyzer (TMA-60 H Shimadzu). The sample shaped like a disc (5 mm diameter) using a paper puncher. The heating rate was 10°C/min under Nitrogen atmosphere flow rate of 30 mL/min.

#### 2.3.11. Contact angle measurements

Static water contact angle measurements were performed at room temperature using (Advanced Goniometer model 500-F1) in a sessile drop configuration (using ultra-pure water as the liquid), coupled with a video camera and image analysis software.

#### 2.3.12. Calculation of the membrane's efficiency

Evaluation of PEMFC performance can be obtained with the following expression:

$$E = \frac{C}{P} \quad (5)$$

where  $E$  is the overall membrane performance,  $C$  is the ionic conductivity, and  $P$  is the methanol permeability.

Efficiency factor ( $E$ ) is another indicator where the IEC was an indicator of the ionic conductivity and calculated according to the following equation:

$$E = \frac{\text{IEC}}{P} \quad (6)$$

### 3. Results and discussion

In the present study, two categories of PEMs were prepared based on the interaction between the alginate matrices and the sulfonated chitosan. The first category results from ionic interaction between the alginate and the sulfonated chitosan to have physically SC/Alg PEMs. On the other side, covalent interaction between the glutaraldehyde activated alginate and the sulfonated chitosan, in addition to the ionic interaction, to have chemically SC/AlgG PEMs as the second category.

According to the proposed sulfonation mechanism in Fig. 2, the sulfonation takes place with amine groups. That means less number of remaining amine groups with high sulfonation degree. On the other hand, the sulfonated chitosan derivatives kept their hydroxyl groups.

For better understanding, the interaction between the two parent polymers components of the developed SC/Alg PEMs and SC/AlgG PEMs has to be declared.

In the first step, the alginate membrane dried before soaked in calcium chloride solution or glutaraldehyde-calcium chloride solution. At this point, two processes occurred in parallel. The first process is the swelling of the alginate membrane surfaces followed by penetration of water molecules to the interior bulk of alginate. Parallel to that, the calcium ions dissolved in water start the ionic crosslinking process between the carboxylic groups in the same manner starting from the outer two surfaces to the interior bulk of the membrane. Due to the fast rate of the ionic crosslinking step relative to the swelling one, a gradient of the ionic crosslinking takes place with a high degree from the membrane's surfaces to less one towards the bulk of the membrane. This step consumes a portion of the alginate's carboxylic groups and creates another gradient of free carboxylic groups starts high from the membrane's bulk to its lower concentration on the surfaces (Fig. 4).

In the case of glutaraldehyde-calcium chloride solution, a second chemical crosslinking process occurs, in addition to the ionic one. The higher concentration of GA molecules exists in the interface between the GA solution and the membrane's surfaces where, kinetically, GA molecules attached from one side to one hydroxyl group and kept free the second aldehyde side. With the diffusion of GA molecules towards the membrane's bulk, a gradient with less concentration was available where increases the possibility of chemically crosslinked between the alginate chains hydroxyl groups. That creates a gradient of high chemical crosslinking from the membrane's bulk towards less one at the surfaces in contrary to the formed ionic crosslinking; Fig. 4.

In the second step, the dry alginate and the dry GA activated alginate membranes developed in the first step soaked in the sulfonated chitosan solutions. The sulfonated chitosan with three sulfonic contents used in this step is completely water-soluble within the used concentration; 2% solution.

In the first category, where the Ca-alginate ionic crosslinked membrane soaked in the sulfonated chitosan solutions, the remaining protonated amine groups in the sulfonated chitosan interact with the remaining anionic carboxylic groups in the alginate via ionic bonds to have physically SC/Alg PEMs. That interaction that happened in a gradient manner starts high from the bulk where the higher concentration of free alginate carboxylic groups exist to the lower one at the outer surfaces where a minimum number of free alginate carboxylic groups present. It is worthy to mention here that a gradient of polyelectrolyte formation with different compositions will result through the thickness of the membranes where the Alg:SC ratio in favor of alginate at the membrane surface and in favor of sulfonated chitosan in the membrane bulk; Fig. 4.

In the second category (the chemically SC/AlgG PEMs), in addition to the ionic bonds, the interaction was supported with covalent Schiff base bonds between the glutaraldehyde terminals on the glutaraldehyde activated alginate and the amine groups of the sulfonated chitosan. The case here is different where the maximum number of free aldehyde terminals is located on the membrane surface, so the covalently bonded sulfonated chitosan concentration gradient is in a reverse manner to the ionic ones where its



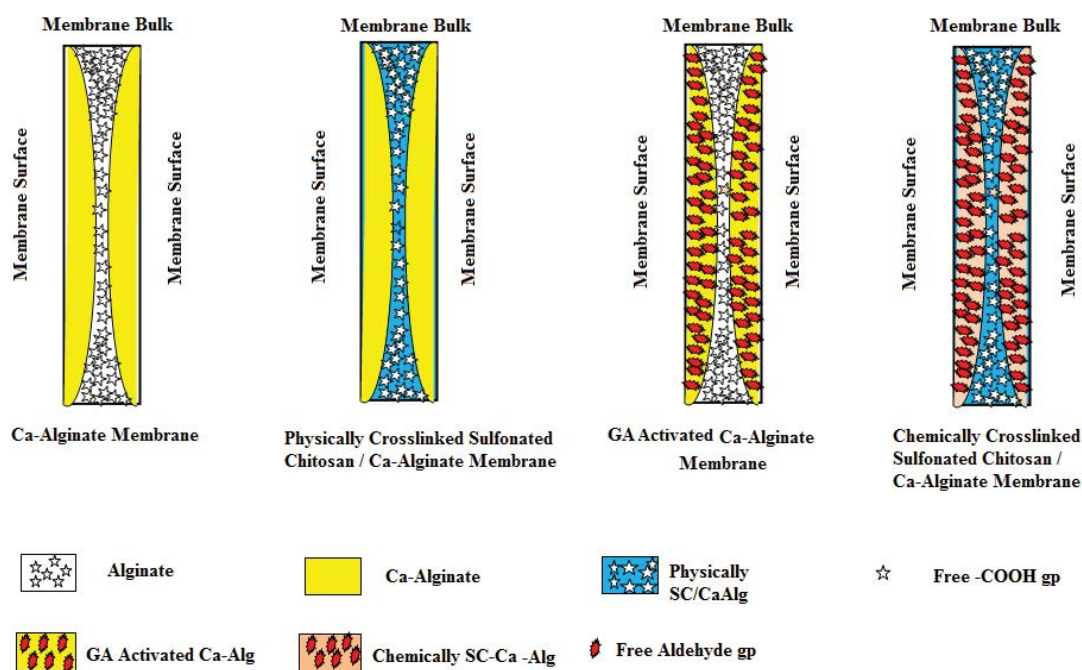


Fig. 4. Proposed interaction mechanisms between Ca-alginate and sulfonated chitosan (physically SC/Alg PEMs) and GA-activated Ca-alginate and sulfonated chitosan (chemically SC/AlgG PEMs).

maximum concentration located in the membrane bulk; Fig. 4.

The prepared membranes were characterized by different analyses related to their chemical structure, physico-chemical properties, and thermal properties. Finally, their methanol permeability was measured and correlated with their IEC to evaluate their efficiencies as probable PEM candidates in the direct methanol fuel cell.

### 3.1. Materials characterization

#### 3.1.1. Elemental analysis

Both chitosan (Ch) and SC samples were analyzed using the elemental analyzer to determine the content percentage of C, N, and S elements in the sample, as presented in Table 1. As the molar ratio of propane sultone to the glucosamine units of chitosan increases, the C/N ratio also increases. Furthermore, the sulfur contents increased gradually from 5.11% to 8.90% compared to the native Ch (0.0%). The increase of sulfur content and the decline of N and C contents proof of the sulfonation process.

#### 3.1.2. FTIR analysis

Fig. 5a shows the FTIR spectra including the characteristic bands of the Ch and SC with different molar ratios [33,34] revealing the presence of sulfonic groups in the modified chitosan. A comparison of the FTIR spectra of Ch with that of SC shows differences between their absorbance bands at  $1,638\text{ cm}^{-1}$  (amide I) and  $1,560\text{ cm}^{-1}$  (amide II). The prove of the sulfonation process recognized in the shift of the band at  $1,560\text{ cm}^{-1}$  (amide II) of chitosan to  $1,532\text{ cm}^{-1}$ . This indicates the involvement of the chitosan'

Table 1  
Sulfur contents and C/N ratios for Ch and different SC molar ratios

Sample code	N%	C%	H%	S%	C/N ratio (%)
Ch	7.21	38.93	6.613	0.0	5.4
SC0.5	5.03	34.74	6.409	5.116	6.9
SC1	4.26	33.25	6.347	7.483	7.8
SC2	3.38	31.20	6.398	8.902	9.23

amino groups in the sulfonation reaction through forming secondary amid groups. On the other hand, Ch and SC represent hydrophilic groups as  $-\text{OH}$  and  $-\text{NH}_2$ , which exhibit strong hydrogen interactions, demonstrating broadband at  $3,300\text{--}3,400\text{ cm}^{-1}$ . Furthermore, it was observed that these peaks were sharpened in the case of sulfonated chitosan because the strength of the hydrogen interaction decreased with the degree of sulfonation and the overlapping between  $-\text{OH}$  and  $-\text{NH}_2$  absorption decreased following sulfonation with 1,3-propane sultone. The  $-\text{OH}$  position became evident, sharp, and shifted from  $3,363$  to  $3,406\text{ cm}^{-1}$ .

The FTIR spectra for the physically SC/Alg and chemically SC/AlgG PEMs, with different substations of sulfonic groups, are shown in Fig. 5b and c. The stretching vibration of sulfoxide in sulfonic acid at both  $1165\text{--}1,150$  and  $1,350\text{--}1,340\text{ cm}^{-1}$  [33,34] revealing the presence of sulfonic groups in the sulfonated chitosan component appeared especially at high sulfonated degree membranes in addition to the stretching vibration of C–H group in the sulfonic acid at  $2,900\text{ cm}^{-1}$ . The alginate membrane exhibits characteristic functional groups ( $\text{COO}^-$  stretching) with a narrower symmetrical band at  $1,409\text{ cm}^{-1}$ , a broad asymmetrical band at

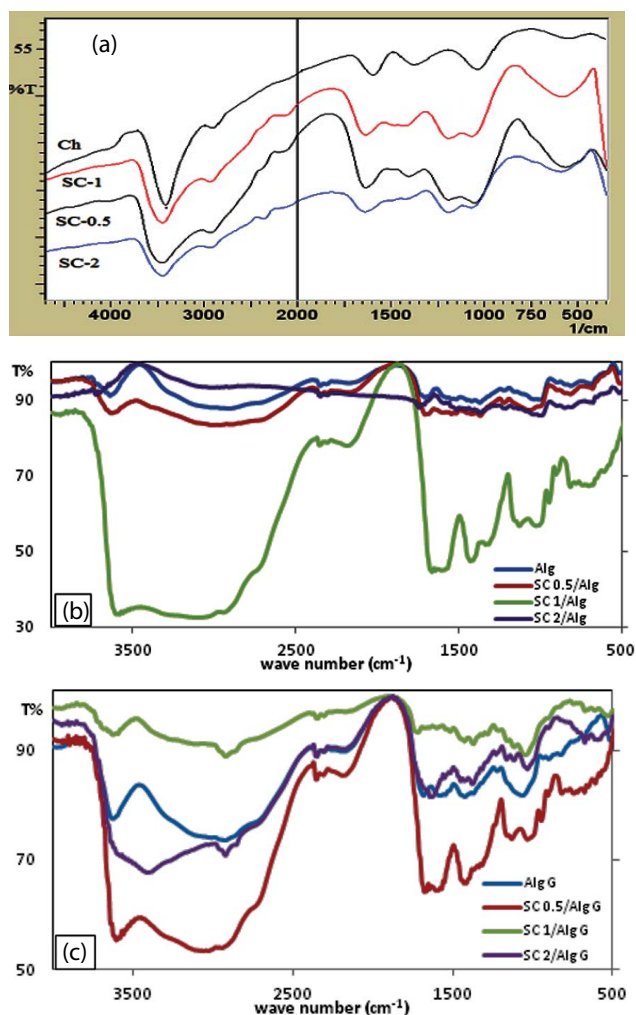


Fig. 5. FTIR spectra of Ch and different SC molar ratios (a), the alginate-sulfonated chitosan prepared membranes; physically SC/Alg (b) and chemically SC/AlgG (c).

1,670  $\text{cm}^{-1}$  and a narrower symmetrical band at 1,409  $\text{cm}^{-1}$ . In addition, the bands around 1,320  $\text{cm}^{-1}$  (C–O stretching), 1,130  $\text{cm}^{-1}$  (C–C stretching), 1,090  $\text{cm}^{-1}$  (C–O stretching), 1,020  $\text{cm}^{-1}$  (C–O–C stretching), and 950  $\text{cm}^{-1}$  (C–O stretching) are attributed to its saccharide structure [35]. The physically SC/Alg PEMs demonstrate main vibration modes; asymmetrical and symmetrical bending  $\text{NH}_3^+$  vibrations at 1,620, 1,596 and 1,421  $\text{cm}^{-1}$ . The chemical glutaraldehyde activated the sharpening of the bands evidenced alginate-sulfonated chitosan formation at 1,670  $\text{cm}^{-1}$  due to the  $\text{COO}^-$  groups in the alginate and the disappearance of the SC amino band at 1,596  $\text{cm}^{-1}$ . Also, the appearance of a small peak was observed at around 1,080  $\text{cm}^{-1}$ , possibly as a result of ionic interactions between the  $\text{COO}^-$  groups and  $\text{NH}_3^+$  groups.

### 3.1.3. Thermal gravimetric analysis

Fig. 6a shows the thermal stability behavior Ch and different SC molar ratios. It was clear that both Ch and SC demonstrate three weight loss phases. The first phase begins at 50°C–150°C, which may be attributed

to the evaporation of the moisture content in the samples. Where the moisture content increased from 6.77% (in case of Ch) to 14.28% (in case of SC2), and this refers to increasing of the hydrophilicity of chitosan as a direct result of the sulfonation process. The second phase could be related to the oxidative decomposition of the chitosan backbone. In this stage, the depression was produced from the destruction of amine groups to form crosslinked fragments [34]. The third phase was observed at the higher temperatures and could be attributed to the decomposition of a new cross-linked adduct. Furthermore, the temperature required for Ch to lose its half weight ( $T_{50}$ ) was 481.5°C. While it decreased in the case of the sulfonated samples and reached 290.08°C for the higher sulfonation degree (SC2). These results indicate that the thermal stability of Ch was decreased after the process of sulfonation.

Fig. 6b and c represent the thermal gravimetric analysis of alginate base membranes that interacts physically and chemically with sulfonated chitosan. In general; both sets exhibit the same degradation behavior. Elevated temperature distinguished degradation steps were recognized. The dehydration of entrapped water molecules associated with the hydrophilic groups (hydroxyl, amine, sulfonic and carboxylic) for physically SC/Alg formed membranes, samples loss 18.03%, 18.24%, 19.39% and 17.75% of Alg, SC0.5/Alg, SC1/Alg, and SC2/Alg membranes, respectively at a temperature up to 150°C (Fig. 6b). Chemically formed SC/AlgG ones show a few less hydrophilicity where moisture loss was 16.58, 17.53, 18.14 and 16.57 for AlgG, SC0.5/AlgG, SC1/AlgG and SC2/AlgG, respectively. This appearance can be described by the loss of part of hydrophilic groups (hydroxyl or amine) in the crosslinking process (Fig. 6c). Raised temperature exhibits the second degradation step that starts from 220°C; that was attributed to the oxidative degradation of pyranose ring in the polysaccharide backbone [36–38]. For physically SC/Alg PEMs, the second degradation phase ends at temperature ranged from 300°C to 315°C where differentiation based on the degree of sulfonation was observed. While the chemically SC/AlgG PEMs end their second degradation phase at 310°C with no differentiation observed. The third degradation level was observed at the higher temperature as a result of degradation of the formatted adduct. One of the characteristic features to distinguish between the two developed PEMs types is the  $T_{50}$  which refers to the temperature at which the matrix losses 50% of its weight. Table 2 demonstrates the  $T_{50}$  of parent polymers and the developed PEMs. For physically SC/Alg one, the recognized  $T_{50}$  decreased with the sulfonation degree of the chitosan component in accordance manner with the  $T_{50}$  of the sulfonated chitosan derivatives. This trend is hard to observe in the case of chemically SC/AlgG PEMs. Such difference in the  $T_{50}$  behavior between the physically SC/Alg and chemically SC/AlgG PEMs may be referred to as the type of interaction between the parent polymers in each type. The ionic interaction is the only interaction between the alginate' carboxylic groups and the remaining amine groups of sulfonated chitosan derivatives in the case of the physically SC/Alg PEMs as suggested in Fig. 1. On the other hand, covalent bonds between the free GA terminals of the GA-activated alginate and the

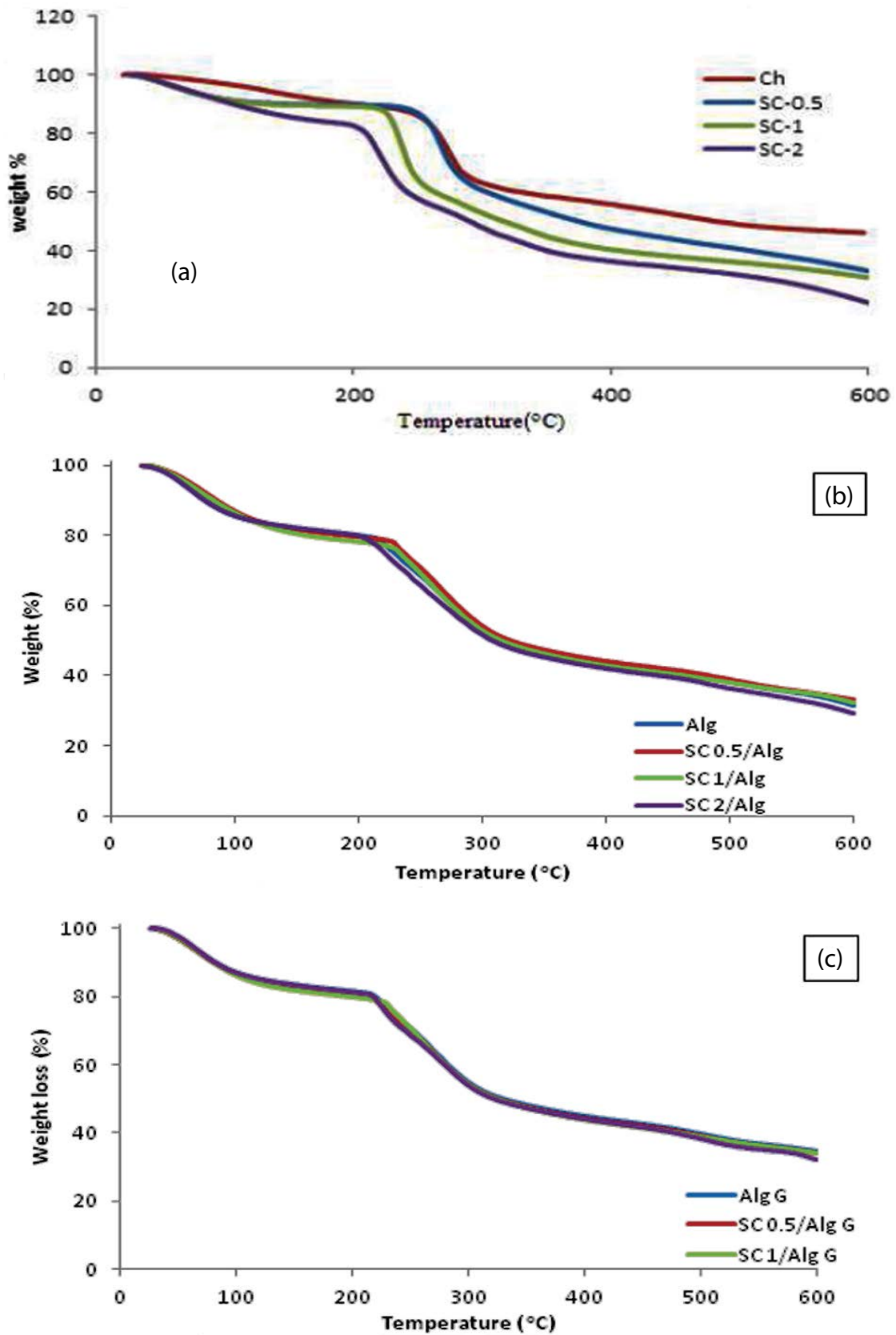


Fig. 6. TGA of the Ch and SC of different molar ratios (a), physically SC/Alg PEMs (b), and chemically SC/AlgG PEMs (c).



Table 2  
T<sub>50</sub> of parent polymers and developed PEMs

Sulfonated chitosan		Physically SC/Alg PEMs		Chemically SC/AlgG PEMs	
Ch	457°C	Alg	318.5°C	AlgG	328°C
SC0.5	362°C	CS0.5/Alg	323.6°C	CS0.5/AlgG	325°C
SC1	310°C	CS1/Alg	316.6°C	CS1/AlgG	324°C
SC2	286°C	CS2/Alg	309.1°C	CS2/AlgG	324°C

remaining amine groups of the sulfonated chitosan derivatives are predominant in the case of the chemically SC/AlgG PEMs in addition to the ionic interaction as suggested in Fig. 1.

#### 3.1.4. X-ray diffraction analysis

XRD patterns of pure Ch and SC with different molar ratios were observed and shown in Fig. 7a [36]. On the other hand, the crystallinity of SC decreased compared to the native Ch, and the appearing peak at  $2\theta = 11^\circ$  in the case of Ch was shifted to lower  $2\theta$  values. This result could be explained by the fact that the disordered structure prevents the polymer from absorbing more water and/or the loss of hydrogen bonding through the sulfonation process. These observations were similar to the previous results, which indicate that the crystallinity of chitosan decreases after the N-alkylation process due to the introduced alkyl groups [39,40]. In the case of the alginate sulfonated chitosan membranes interact physically and chemically with different substations of the sulfonic group, XRD patterns have been analyzed in the  $2\theta$  range of  $5^\circ$  to  $50^\circ$  as displayed in Fig. 7b and c. It was noted that the polyion complex membrane resembled to have higher amorphous morphology than that of sodium alginate. It is remarked that a crystalline peak of sulfonated chitosan at  $2\theta = 10^\circ$  in SC/Alg disappeared as the polyion complex was formed between sodium alginate and chitosan, which is attributed to the exclusion of hydrogen bonding between hydroxyl groups and amino groups in chitosan [41].

#### 3.1.5. Morphological characterization

The chemical modification of the chitosan structure always reflects on its morphological characters. It was evident from Fig. 8a that the morphological structure of Ch differed after the sulfonation process, in which it converted from the granular structure to a flat structure (SC2). These changes could be due to the ionic bonds of the introduced sulfonic groups. The morphological modification of sulfonated chitosan/alginate membranes that interacts chemically or physically with different substations of alkyl sulfonic groups was represented in Fig. 8b and c. It was evident from the figure that the morphological structure of the formed membranes was become rougher by interacting with sulfonated chitosan. This action was strengthened with an increase of the chitosan sulfonation degree. Additionally, the chemically formed alginate-sulfonated chitosan membranes are rougher than physical ones. No phase separation has been observed in any of the formed

PEMs. That observation indicates that both polymers are very homogeneously intermixed during the formation of both polyion complexes. Moreover, open cavities have been observed on the surface of the sulfonated chitosan/alginate membranes interact chemically or physically. These cavities are probably formed as a result of the micro air bubbles traveled to the membrane's surface during the cross-linking process and drying of the membranes. The bubbles are more clearly observed on the chemically crosslinked alginate/sulfonated chitosan membranes.

### 3.2. Polyelectrolyte membranes evaluation

#### 3.2.1. Water uptake and wettability

The water uptake or content of any polymer is governed by many factors. The hydrophilic function groups' content and the structure porosity come first. Based on that, both developed PEMs types in this study possess hydrophilic groups and have a certain degree of porosity based on the ionic crosslinking in case of the physically SC/Alg PEMs and on the overlapping between the ionic and covalent crosslinking in case of chemically SC/AlgG PEMs. Accordingly, the water content of both developed PEMs types is divided into two categories. The first one is the water molecules attached through hydrogen bonds with the hydrophilic group's content, while the second category is the water molecules that fill the pores of the polymer matrix.

Fig. 9 shows the water uptake (%) of the physically and chemically PEMs in addition to the alginate and GA-activated alginate base membranes. Two observations were extracted from the figure. The first observation concerns the reduction of the water uptake (%) of the developed PEMs with an increase of the chitosan component' sulfonation degree. The second observation referred to the lower water uptake (%) of the chemically SC/AlgG PEMs. To understand better, it is worthy to mention that the SC derivatives are water-soluble and the increase in the sulfonation degree resulted in an increase in the "volume" of the sulfonated chitosan molecules and their negative charges in addition to the protonation of the remaining amine groups.

In the case of the physically SC/Alg PEMs, the hydrophilic groups present are hydroxyl, carboxylic, amine and sulfonic. It was expected to have a water uptake (%) increment with an increase in the sulfonation degree of the SC component due to attaching more water molecules. However, this expectation was compromised by reduction of the water molecules numbers filled the membrane's bulk section which is already occupied by the SC molecules; Fig. 4. That explanation is confirmed by the linear

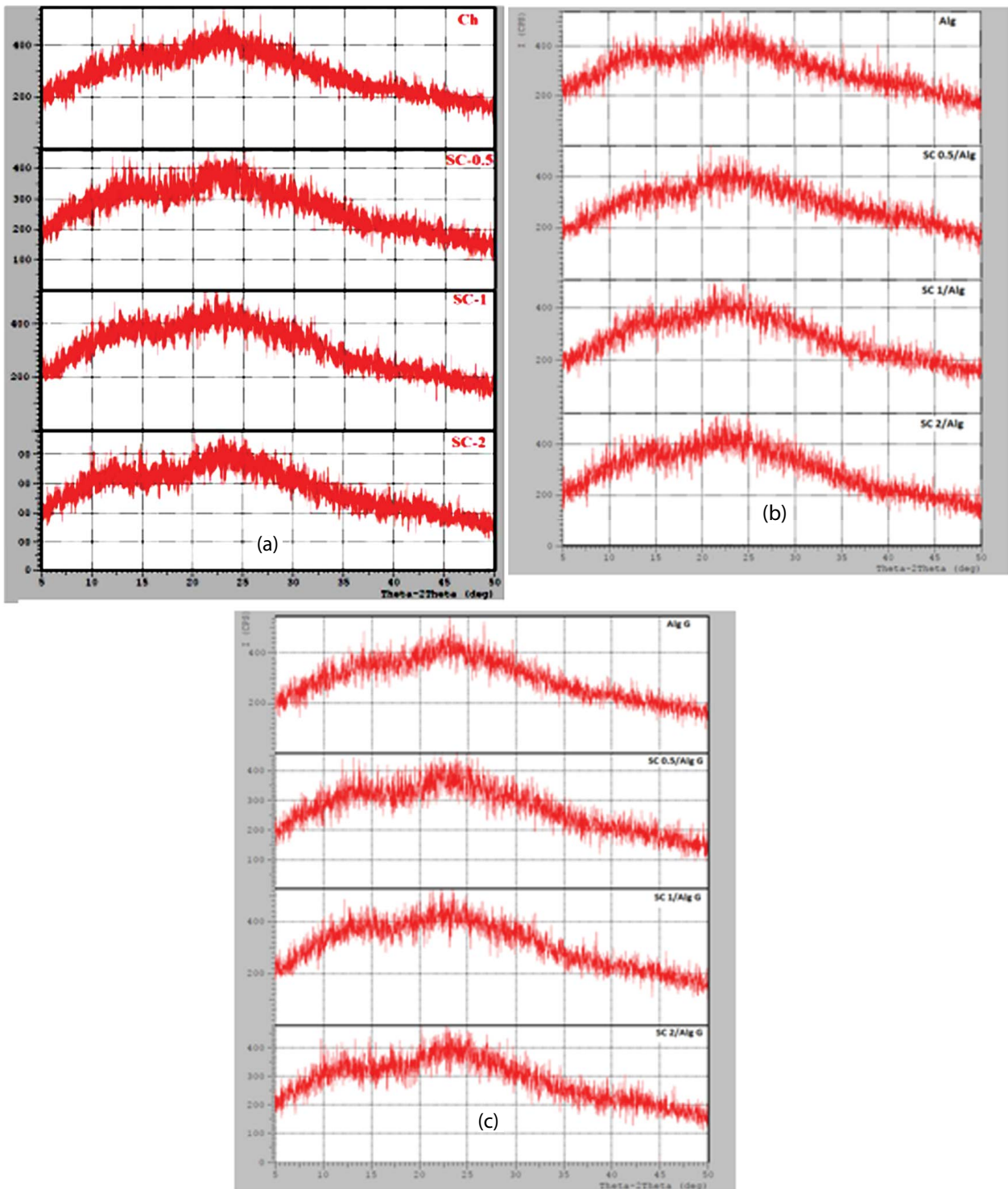


Fig. 7. XRD of Ch and different SC molar ratios (a), physically (b), and chemically SC/AlgG (c) membranes.

and gradual decrease behavior of the water uptake (%) of the physically SC/Alg PEMs with sulfonation degree of SC component.

On the other hand, the water uptakes (%) of the chemically SC/AlgG PEMs show lower values. That could be explained partially by the reduction of the voids volume

in the membrane’s bulk section as mentioned in the case of the physically SC/Alg PEMs in addition to further reduction caused by the postulated GA chemical crosslinking as shown in Fig. 4. Furthermore, the additional chemical interaction between the free GA terminals on the membrane’s surface and the sulfonated chitosan molecules create

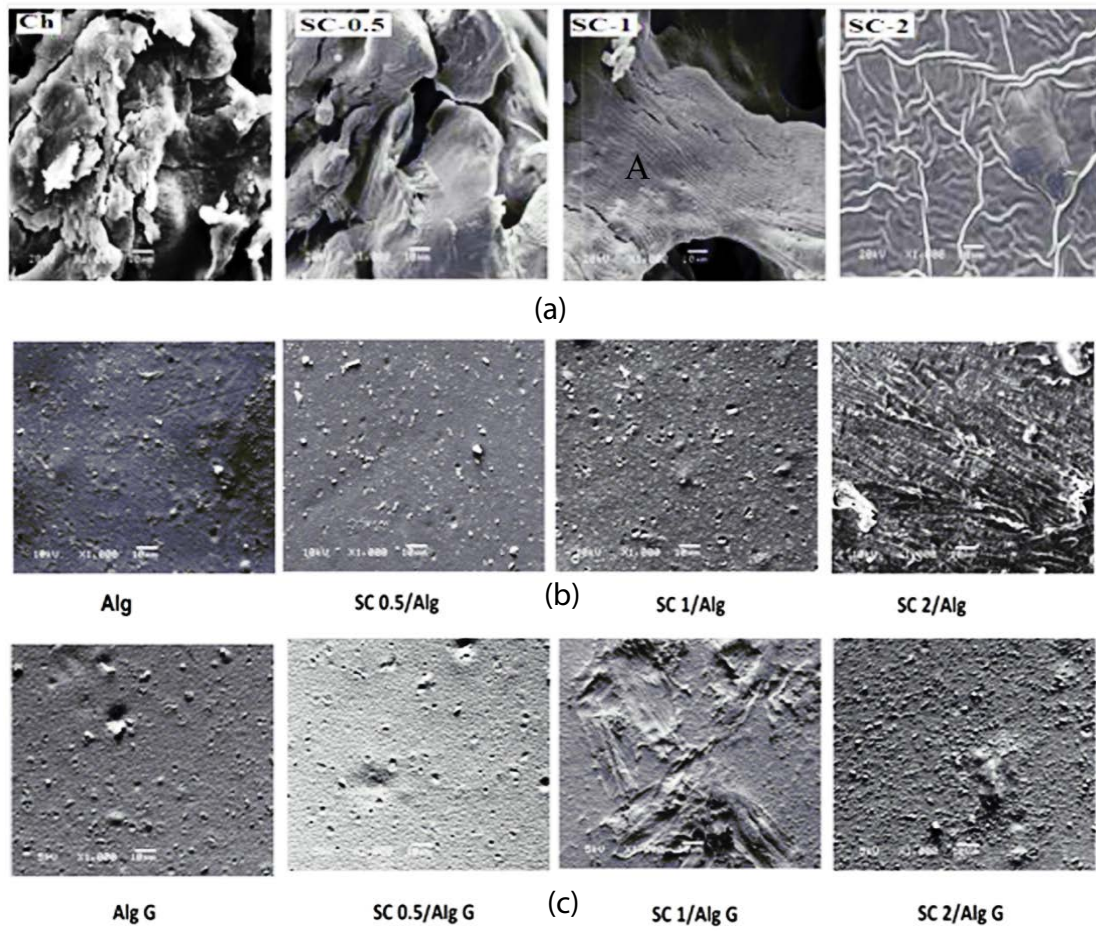


Fig. 8. SEM images of the Ch and different SC molar ratios (a), physically SC/Alg (b), and chemically SC/AlgG (c) formed membranes.

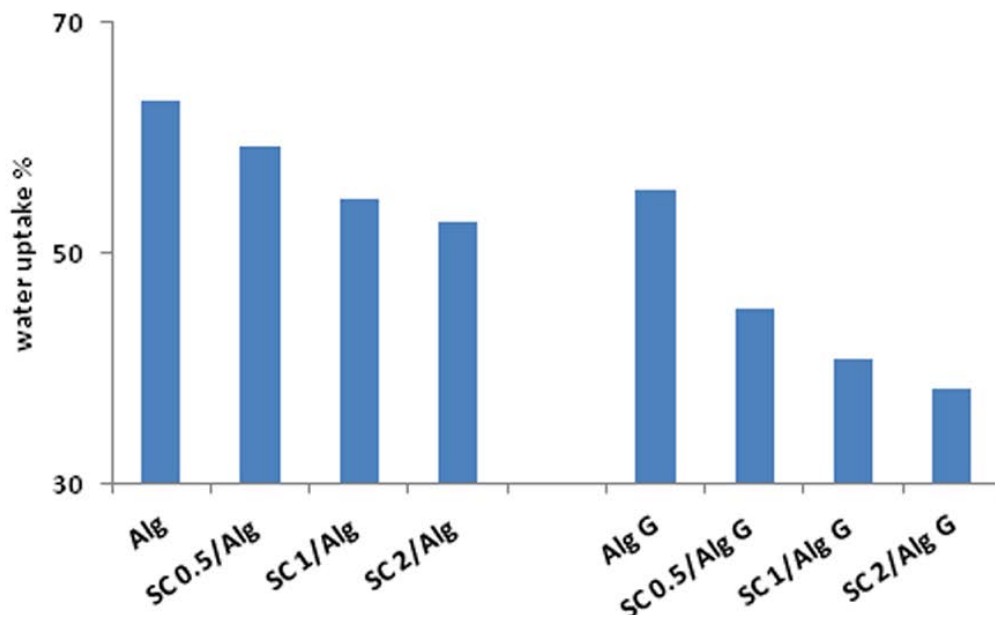


Fig. 9. Water uptake of physically SC/Alg and chemically SC/AlgG polyelectrolyte membranes.

additional barrier block the way and retard the diffusion of water molecules to the membrane's interior. The effect increases gradually and linearly with an increase in the sulfonation degree of the SC component and in a higher reduction percentage compared with the physically SC/Alg PEMs counterparts.

These results are in agreement with the obtained results by Wafiroh et al. [42] where they developed sulfonated chitosan-sodium alginate composite membrane as proton exchange membrane fuel cell (PEMFC) where they performed sulfonation process for both parent polymers components. Accordingly, the reduction of filling water molecules number is more visible regarding the high formed number of sulfonated groups all over the membranes.

Different results were found by Pasini Cabello et al. [23] where they replaced the sulfonated chitosan with carrageenan for the development of novel polyelectrolyte membranes. They found that the water uptake increases with an increase in the Car content. That behavior may be referred to as the absence of alginate' carboxylic group's engagement in the ionic crosslinking process, accordingly, they are free and available for attaching with more water molecules.

Our assumption about the chemical interaction between the GA activated alginate, at the membrane's surface, and the SC confirmed by the contact angles measurements as a reflection of the membrane's surface wet-ability depend on the topographical micro-structure and the surface chemical composition. Table 3 presented the gained contact angle results for the chemically SC/AlgG membranes. The results clarified that the wettability of the developed membranes improved compared with the native chitosan where the maximum water-contact angle value was 53.37° and recorded by the CS2 sample compared to 75.12° for neat chitosan (Ch). These observations ascribed to increasing the sulfonic group density, which in turn leads to increasing the hydrophilicity of the developed membrane's surface, regardless of the reduction of the water uptake and in accordance with the developed chemically SC/AlgG PEMs proposed structure presented in Fig. 4.

### 3.2.2. Ion exchange capacity of the membrane

The IEC values for Ch and the sulfonated chitosan derivatives prepared under different SC molar ratios were investigated in Fig. 10a. Results demonstrated that the IEC values increased gradually and reached a maximum value (2.62 meq/g) with increasing the used amount of 1,3-propane sultone from 5 mM (SC0.5) to 20 mM (SC2) in comparison with the native Ch (0.092 meq/g). This observation could be related to increasing the induced sulfonic groups

responsible for increasing the IEC of the resultant SC derivatives.

Fig. 10b illustrates the IEC of the physically and chemically interacted alginate-sulfonated chitosan PEMs. The significant increase of the IEC with increasing the degree of chitosan sulfonation was referred to as the potential of the induced sulfonic groups. Also, it was observed from the figure, the increase of the IEC of the chemically formed membranes compare to the physical ones. Such increment could be attributed to more than one factor which works individually or in synergetic effect. These factors can be summarized as follow;

- Increase the SC content as a result of additional covalent SC molecules on the membrane's surface,
- The formed Schiff base between the GA activated alginate and the chitosan amine groups [43],
- Improved the distribution of the sulfonic groups through membrane thickness.

Such behavior of the IEC increment with the sulfonation degree of SC is in agreement with other published results [23,42].

### 3.2.3. Methanol permeability measurement

Methanol crossover is one of the most defects in the methanol fuel cell. Permeation of methanol through polymeric membranes to anode limits cell productivity. Table 4 represented the change in the methanol permeability of the alginate base membranes and their polyelectrolyte complexes with sulfonated chitosan (SC2). Some important information can be extracted from the tabulated results. The first information indicates that the methanol permeability of the GA-activated alginate membrane is 19% lower than the alginate membrane. This observation confirmed the benefits of using the GA-activated alginate as a base polymer to develop PEMs for FC applications. The second information indicates the reduction of the methanol permeability of the chemically SC/AlgG PEMs by 26% regard to the physical ones. That observation indicates the success of the sulfonated chitosan derivatives in the contribution to the reduction of the methanol permeability [42]. And is in accordance with the proposed contribution of GA in the chemically SC/AlgG PEMs which proposed a secondary role in crosslinking of alginate matrix; Fig. 4.

These results are in agreement with the obtained results by Wafiroh et al. [42] while contradicting the results found by Pasini Cabello et al. [23] where they found that the apparent permeability of methanol for sulfonated Alg/Car membranes increases with the carrageenan content, presumably due to the increase of water content resulted from increasing the hydroxyl free groups in the Car component.

### 3.2.4. Mechanical characteristics

The tensile properties for the physically SC/Alg and chemically SC/AlgG developed PEMs were done and listed in Table 5. It was found a decrease in both stress and strain percent of the PEMs by increasing the sulfonation degree

Table 3  
Contact angle measurements for the chemically SC/AlgG PEMs

Membrane sample	Water-contact angle ( $\theta$ )
Ch	75.12
SC0.5/AlgG	68.37
SC1/AlgG	62.54
SC2/AlgG	53.37



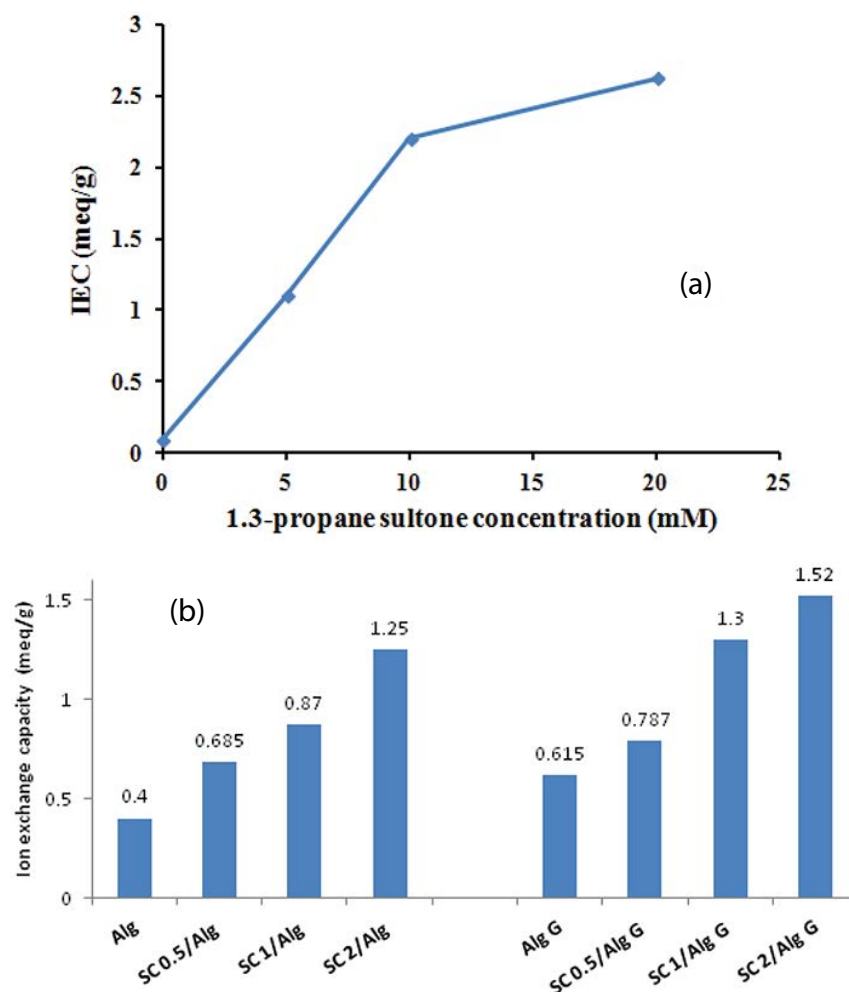


Fig. 10. The ion exchange capacity of the Ch and different SC molar ratios (a) and the alginate-sulfonated chitosan membranes interact chemically and physically with different substations of the sulfonic group (b).

Table 4  
Methanol permeability of the alginate, GA activated alginate, and the physically SC/Alg and chemically SC/AlgG developed PEMs

Membrane	Methanol permeability ( $\text{cm}^2/\text{s}$ )
Alg	$1.918 \times 10^{-9}$
SC2/Alg	$2.830 \times 10^{-9}$
AlgG	$1.556 \times 10^{-9}$
SC2/AlgG	$2.1019 \times 10^{-9}$

of the chitosan component. That may be attributed to the consumption of the amine groups in the sulfonation process. On the other hand, the presence of glutaraldehyde as a covalent crosslinker has not a clear role in support of the chemically SC/AlgG formed PEMs mechanical properties. However, the chemically SC/AlgG formed PEMs become more brittle compared to the physically SC/Alg formed PEMs ones due to the formation of additional covalent interaction between the GA free terminals on the membrane's surface and the SC.

Thermo-mechanical analysis of the chemically SC/AlgG formed PEMs was performed to mimic the operational conditions in FC, and the results were shown in Fig. 11. From Fig. 11, it is clear that the thickness of the chemically SC/AlgG formed PEMs has been reduced under constant load (5.0 g) and varying of the temperature up to  $120^\circ\text{C}$ . The highest reduction of the thickness of the membranes (compactness) noticed with the membrane of the highest sulfonation degree (CS2) and is expected to have a positive impact on the reduction of the methanol permeability and the increase of the ionic conductivity due to shortening the bath of ions transfer from the anode to the cathode side.

### 3.2.5. Membrane efficiency and comparison

The efficient PEMFC must have high ion exchange capacity because the membrane with high IEC has the excellent potential to deliver the proton from anode to cathode [44] and low methanol crossover permeability for high cell productivity.

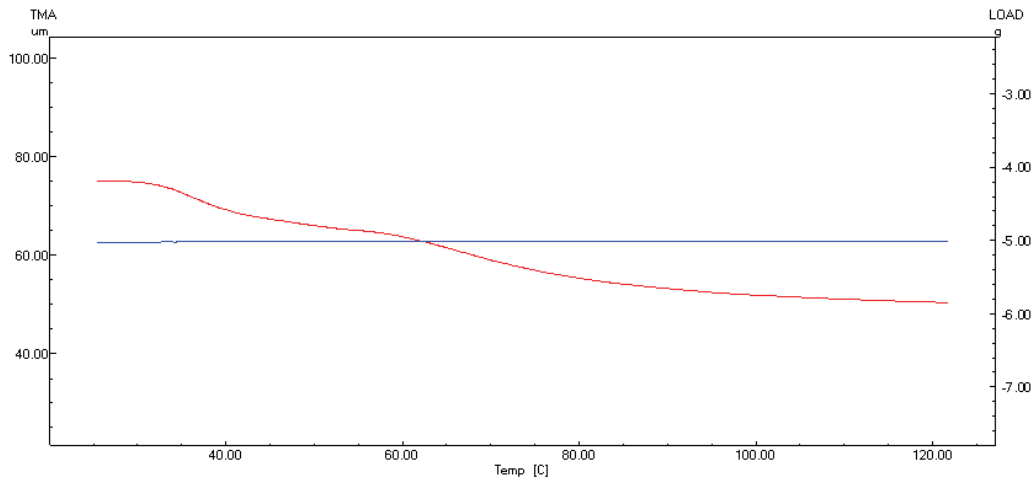
The evaluation of the efficiency of the modified membranes was performed according to Eq. (6) [45], and



Table 5  
Mechanical parameters of the physically and chemically formed alginate-chitosan sulfonated PEMs

Sample	Max force (N)	Max displacement (mm)	Max stress $\sigma_{max}$ (N/mm <sup>2</sup> )	Max strain $\lambda_{max}$ (%)
Alg	36.72	2.39	143.99	11.95
SC0.5/Alg	27.97	0.86	109.68	4.31
SC1/Alg	21.88	0.84	85.78	4.2
SC2/Alg	19.22	0.92	75.37	4.6125
AlgG	39.53	1.22	97.61	6.08
SC0.5/AlgG	32.81	0.79	81.02	3.965
SC1/AlgG	39.84	1.09	59.03	5.475
SC2/AlgG	17.34	0.48	42.82	2.387

Sample Name:ch  
Sample Length:0.075[mm]  
Atmosphere: Nitrogen  
Flow Rate: 30[ml/min]



Sample Name:ch-s 0.5  
Sample Length:0.086[mm]  
Atmosphere: Nitrogen  
Flow Rate: 30[ml/min]

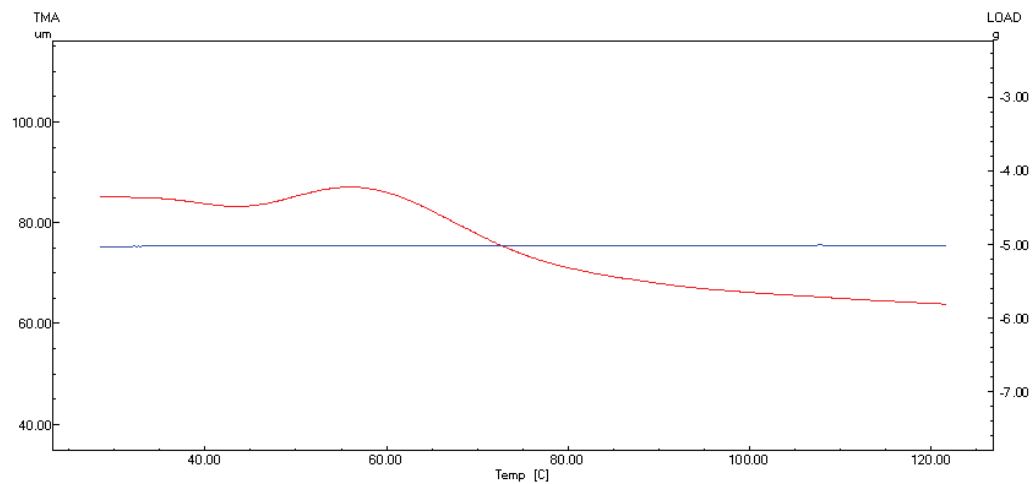
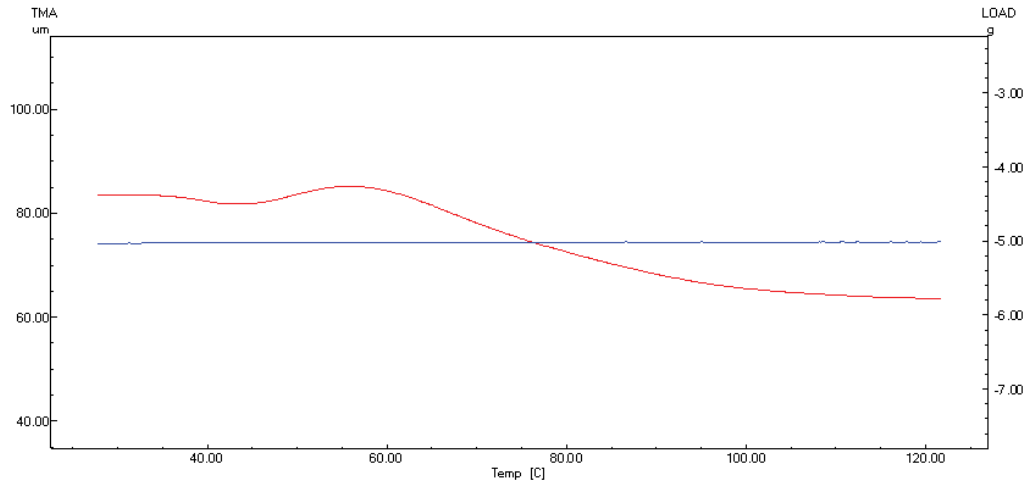


Fig. 11. Continued

Sample Name:ch-s 1  
 Sample Length0.084[mm]  
 Atmosphere: Nitrogen  
 Flow Rate: 30[ml/min]



Sample Name:ch-s 2  
 Sample Length0.096[mm]  
 Atmosphere: Nitrogen  
 Flow Rate: 30[ml/min]

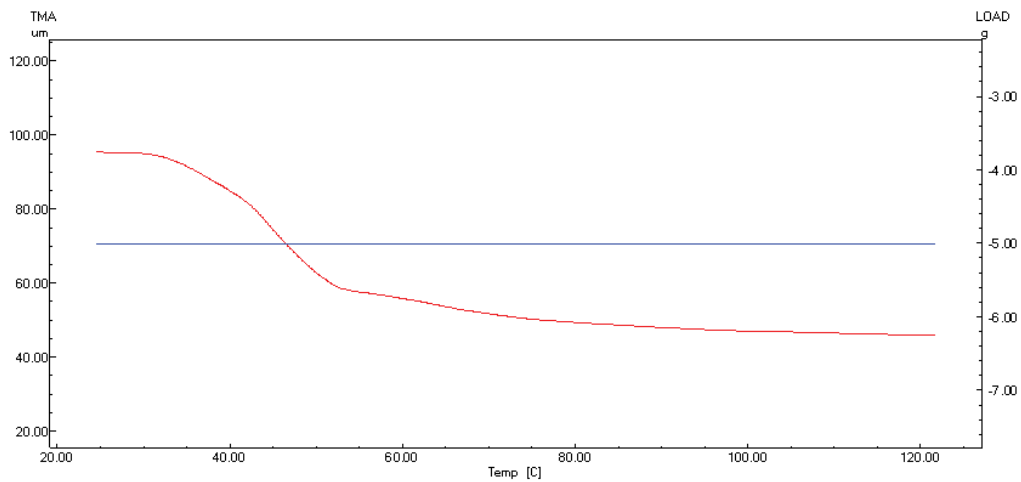


Fig. 11. Thermo-mechanical analysis of the physically SC/Alg and chemically SC/AlgG PEMs with different substations of sulfonic groups.

Table 6  
 Efficiency factor comparison of PEMs

Membrane	IEC (meq/g)	Methanol permeability (cm <sup>2</sup> /s)	Efficiency factor	Reference
Nafion 117	0.9	$1.14 \times 10^{-9}$	$0.7894 \times 10^{-9}$	[29]
Ch/AlgG	5.96	$0.217 \times 10^{-9}$	$27.00 \times 10^{-9}$	[29]
Alg	0.4	$1.918 \times 10^{-9}$	$0.2085 \times 10^{-9}$	This work
SC2/Alg	1.25	$2.830 \times 10^{-9}$	$0.4417 \times 10^{-9}$	This work
AlgG	0.615	$1.556 \times 10^{-9}$	$0.3952 \times 10^{-9}$	This work
SC2/AlgG	1.52	$2.1019 \times 10^{-9}$	$0.7231 \times 10^{-9}$	This work

compared with the virgin Nafion 117 membrane, Table 6. From the presented data, it is obvious the incorporation of the sulfonated chitosan (SC2) has a clear positive impact on the efficiency of both PEMs types where increased by 112% and 83% for the physically SC/Alg and chemically SC/AlgG ones relative to alginate and GA activated alginate base membranes. Furthermore, the chemically SC/AlgG PEM has a 64% of efficiency increment relative to the physically SC/Alg counterpart. That results are expected since the chemically SC/AlgG PEM has higher IEC and lower methanol permeability than the physically SC/Alg one. On the other hand, the chemically SC/AlgG PEM has 92% of the Nafion 117 efficiency factor. It is worthy to mention here that the Ch/AlgG PEMs [28], Table 6, with different compositions, have efficiency factors superior to Nafion 117.

To have such superiority for the sulfonated chitosan/alginate base PEMs, further investigations are under work in our laboratories concerning the optimization of the crosslinking process between the alginate and the sulfonated chitosan. Aminated chitosan derivative, reached with extra amino groups, could be an addition in the right direction to have highly sulfonated aminated chitosan and improves the IEC, reduces the methanol crossover permeability and as a result, improves the efficiency of the PEMs.

#### 4. Conclusion

Polyelectrolyte sulfonated chitosan-alginate base membranes for fuel cell applications have been developed from sodium alginate, glutaraldehyde activated alginate and sulfonated chitosan using physical and chemical cross-linking protocols. The IEC of the developed physically SC/Alg and chemically SC/AlgG PEMs was increased up to 1.25 and 1.52 meq/g with increasing the sulfonic contents of the sulfonated chitosan which is higher than that of Nafion 117. On the other hands, the developed PEMs have relatively higher methanol permeability ( $2.830 \times 10^{-9}$  and  $2.1019 \times 10^{-9}$  cm<sup>2</sup>/s) for physically SC/Alg and chemically SC/AlgG PEMs compared to Nafion® 117 membranes ( $1.14 \times 10^{-9}$  cm<sup>2</sup>/s). Accordingly, the efficiency factor of the chemically SC/AlgG PEMs was almost equal to that of the Nafion 117. These findings implied that the developed polyelectrolyte alginate-sulfonated chitosan membranes could be suitable candidates as low-cost PEMFC and need further investigations to have PEMs superior to the Nafion counterpart.

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